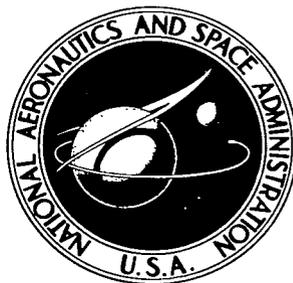


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NASA TN D-4165

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THERMODYNAMIC PROPERTIES OF POTASSIUM TO 2100° K

by Sheldon Heibel

Lewis Research Center

Cleveland, Ohio



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THERMODYNAMIC PROPERTIES OF POTASSIUM TO 2100° K

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Lewis Research Center

SUMMARY

Consistent thermodynamic properties of potassium from the melting point (336.35° K) to 2100° K were computed for both the ideal and the real species and are presented in tabular form.

The properties computed for the real monomeric vapor on the saturation line are as follows: pressure, volume, heat capacity, enthalpy of vaporization and enthalpy, entropy of vaporization and entropy, fugacity-pressure ratio, virial coefficients (second, third, and fourth), compressibility factor, density, partial derivative of volume with respect to temperature at constant pressure, and partial derivative of volume with respect to pressure at constant temperature.

The properties computed for the ideal species (condensed phases, monomeric gas, and dimeric gas) are heat capacity, enthalpy, entropy, and free energy.

The real-gas properties were computed from a virial equation of state. The equation used existing second virial coefficients based on the Rydberg potential. Third and fourth virial coefficients exhibiting limited aspects of hard-sphere behavior were adjusted to experimental pressure-volume-temperature (PVT) data.

INTRODUCTION

Three areas requiring a reliable equation of state of the alkali metals are (1) Rankine-cycle engines, (2) radiation heat transfer in plasmas, and (3) calculation of transport properties. In one study of the Rankine-cycle engine at the Lewis Research Center (ref. 1), an equation of state for potassium was used to calculate the critical weightflow rate in a nozzle.

There are two recent virial equations of state for potassium (refs. 2 to 5). These equations yield discrepant sets of thermodynamic properties. Therefore, the present work was performed to eliminate the discrepancies by presenting an improved equation. The improvement lies in the representation of each virial coefficient (up to the fourth) by the "best" available potential model.

Second virial coefficients derived from the Rydberg potential (1100^o to 1600^o K) were taken from reference 6. The dependencies of the third and fourth virial coefficients on the second virial coefficient were taken from the hard-sphere model (ref. 7). These dependencies correlate the experimental volumes (1127^o to 1575^o K) (refs. 2 to 4) better than analogous dependencies from the Lennard-Jones 12-6 potential (ref. 8).

Analytic functions approximating the virial coefficients were used in the range from 336.35^o to 2100^o K in order to extend the range of the equation of state beyond the range of the pressure-volume-temperature (PVT) data. In addition, smoothed vapor pressures over the entire experimental range of 372^o to 2078^o K (refs. 2 to 4, 9 to 11, and unpublished data of K. J. Bowles of Lewis) were used. The justification for this procedure is the reasonable trend shown by calculated heat capacities, fugacity-pressure ratios, and compressibility factors.

The results of the analysis are as follows:

(1) An improved equation of state is obtained for the temperature range 336.35^o to 2100^o K.

(2) Volumes, heats of vaporization, and isentropic expansion indexes derived from the equation are in good agreement with experimental data.

Tables of thermodynamic functions are presented for the ideal crystal, liquid, monomer, and dimer and for the real monomer on the saturation line.

THERMODYNAMIC PROPERTIES OF IDEAL SPECIES

The thermodynamic properties of the condensed phases (crystal and liquid) and of the monomeric and dimeric gases are given in tables I, II, and III, respectively. These properties were obtained in the following manner.

Crystal

The JANAF data (ref. 12) for the heat capacity at constant pressure for the standard state C_p^o , the sensible enthalpy for the standard state $H_T^o - H_0^o$, the entropy for the standard state S_T^o from 100^o to 300^o K were extrapolated to the melting point by the Lagrangian formula. (Superscript letter o indicates the ideal state. All symbols are defined in appendix A.) The melting point (336.35^o K) and the heat of fusion of 558 calories per mole (2334.67 J/mole) were taken from Douglas et al. (ref. 13).

The arbitrary base for assigning values to the enthalpy of crystal and liquid potassium (K) was a value of zero at 298.15^o K (i. e., $(H_{298.15}^o)_c = 0$). Since table I gives $(H_{298.15}^o - H_0^o)_c$ as 1693.0 calories per mole (7083.5 J/mole), $(H_0^o)_c = -1693.0$ calories per mole (-7083.5 J/mole).

TABLE I. - THERMODYNAMIC PROPERTIES OF CRYSTAL AND LIQUID POTASSIUM

Temperature, T, °K	Heat capacity for standard state at constant pressure, C_p^0/R	Sensible enthalpy for stand- ard state at T° K, $\frac{H_T^0 - H_0^0}{RT}$	Entropy for standard state, S_T^0/R	Sensible free en- ergy for standard state at T° K, $-\frac{(F_T^0 - H_0^0)}{RT}$	Sum of sensible enthalpy at T° K and chemical energy at 0° K for standard state, H_T^0/RT	Formation from assigned reference state	
						Enthalpy change at T° K, $(\Delta H_T^0)_f/RT$	Log of equilib- rium constant, $\log \mathcal{K}_f$
100	2.9625	2.0834	4.2820	2.1986	-6.4363	0	0
200	3.2478	2.6017	6.4338	3.8321	-1.6581	0	0
298.15	3.5478	2.8575	7.7784	4.9209	.0000	0	0
300	3.5568	2.8617	7.8005	4.9388	.0218	0	0
^a 336.35	3.9624	2.9594	8.2303	5.2709	.4264	0	0
^a 336.35	3.8655	3.7942	9.0651	5.2709	1.2612	0	0
400	3.7885	3.7993	9.7284	5.9292	1.6694	0	0
500	3.6918	3.7870	10.5629	6.7759	2.0830	0	0
600	3.6246	3.7651	11.2296	7.4645	2.3452	0	0
700	3.5870	3.7420	11.7851	8.0431	2.5249	0	0
800	3.5790	3.7218	12.2633	8.5414	2.6569	0	0
900	3.6005	3.7069	12.6858	8.9789	2.7602	0	0
1000	3.6516	3.6985	13.0675	9.3690	2.8466	0	0
^b 1030.90	3.6734	3.6975	13.1789	9.4815	2.8710	0	0
1100	3.7323	3.6977	13.4191	9.7214	2.9232	0	0
1200	3.8425	3.7050	13.7483	10.0434	2.9950	0	0
1300	3.9823	3.7208	14.0612	10.3405	3.0654	0	0
1400	4.1517	3.7453	14.3624	10.6171	3.1368	0	0
1500	4.3507	3.7789	14.6554	10.8765	3.2109	0	0
1600	4.5792	3.8216	14.9433	11.1217	3.2891	0	0
1700	4.8372	3.8736	15.2286	11.3549	3.3725	0	0
1800	5.1249	3.9350	15.5130	11.5780	3.4617	0	0
1900	5.4421	4.0058	15.7985	11.7927	3.5574	0	0
2000	5.7888	4.0862	16.0863	12.0001	3.6602	0	0
2100	6.1652	4.1761	16.3777	12.2016	3.7704	0	0

^aMelting point.

^bNormal boiling point.

TABLE II. - THERMODYNAMIC PROPERTIES OF IDEAL POTASSIUM GAS (K₁)

Temperature, T, °K	Heat capacity for standard state at constant pressure, C _p ^o /R	Sensible enthalpy for standard state at T ^o K, $\frac{H_T^o - H_0^o}{RT}$	Entropy for standard state, S _T ^o /R	Sensible free energy for standard state at T ^o K, $-\frac{(F_T^o - H_0^o)}{RT}$	Sum of sensible enthalpy at T ^o K, and chemical energy at 0 ^o K for standard state, H _T ^o /RT	Formation from assigned reference state	
						Enthalpy change at T ^o K, $(\Delta H_T^o)_f/RT$	Log of equilibrium constant, log K _f
100	2.5000	2.5000	16.5404	14.0404	101.6531	108.0894	-41.6189
200	2.5000	2.5000	18.2732	15.7732	52.0766	53.7347	-18.1949
298.15	2.5000	2.5000	19.2714	16.7714	35.7561	35.7561	-10.5373
300	2.5000	2.5000	19.2869	16.7869	35.5510	35.5292	-10.4417
^a 336.35	2.5000	2.5000	19.5728	17.0728	31.9792	30.7179	-8.7772
400	2.5000	2.5000	20.0061	17.5061	27.2883	25.6189	-6.6626
500	2.5000	2.5000	20.5640	18.0640	22.3306	20.2476	-4.4500
600	2.5000	2.5000	21.0198	18.5198	19.0255	16.6804	-2.9924
700	2.5000	2.5000	21.4052	18.9052	16.6647	14.1398	-1.9629
800	2.5000	2.5000	21.7390	19.2390	14.8941	12.2373	-1.1993
900	2.5000	2.5000	22.0334	19.5334	13.5170	10.7568	-.6120
1000	2.5000	2.5000	22.2968	19.7968	12.4153	9.5687	-.1474
1030.90	2.5000	2.5000	22.3729	19.8729	12.1181	9.2471	-.0231
1100	2.5000	2.5000	22.5351	20.0351	11.5139	8.5907	.2281
1200	2.5001	2.5000	22.7527	20.2526	10.7628	7.7677	.5370
1300	2.5003	2.5000	22.9528	20.4528	10.1272	7.0618	.7946
1400	2.5008	2.5001	23.1381	20.6380	9.5824	6.4457	1.0119
1500	2.5018	2.5001	23.3107	20.8105	9.1103	5.8994	1.1968
1600	2.5034	2.5003	23.4722	20.9719	8.6974	5.4082	1.3552
1700	2.5060	2.5005	23.6240	21.1235	8.3331	4.9606	1.4917
1800	2.5099	2.5009	23.7673	21.2664	8.0095	4.5478	1.6097
1900	2.5154	2.5016	23.9032	21.4016	7.7201	4.1627	1.7120
2000	2.5228	2.5024	24.0324	21.5300	7.4601	3.7999	1.8007
2100	2.5324	2.5036	24.1557	21.6521	7.2252	3.4548	1.8775
2200	2.5446	2.5052	24.2738	21.7686	7.0121	-----	-----
2300	2.5596	2.5072	24.3872	21.8800	6.8182	-----	-----
2400	2.5775	2.5098	24.4965	21.9868	6.6411	-----	-----
2500	2.5988	2.5129	24.6022	22.0893	6.4790	-----	-----

^aThe reference element is crystal potassium below 336.35^o K and liquid potassium above 336.35^o K.

TABLE III. - THERMODYNAMIC PROPERTIES OF IDEAL POTASSIUM GAS (K₂)

Temperature, °K	Heat capacity for standard state at constant pressure, C _p ^o /R	Sensible enthalpy for standard state at T ^o K, $\frac{H_T^o - H_0^o}{RT}$	Entropy for standard state, S _T ^o /R	Sensible free energy for standard state at T ^o K, $-\frac{(F_T^o - H_0^o)}{RT}$	Sum of sensible enthalpy at T ^o K and chemical energy at 0 ^o K for standard state, H _T ^o /RT	Formation from assigned reference state	
						Enthalpy change at T ^o K, $(\Delta H_T^o)_f/RT$	Log of equilibrium constant, log <i>K_f</i>
100	4.3895	3.9898	25.1220	21.1321	142.6636	155.5362	-60.3574
200	4.5137	4.2285	28.2136	23.9851	73.5654	76.8817	-26.7246
298.15	4.5579	4.3303	30.0248	25.6945	50.8417	50.8417	-15.7969
300	4.5585	4.3317	30.0530	25.7213	50.5563	50.5127	-15.6610
^a 336.35	4.5709	4.3569	30.5751	26.2182	45.5859	43.0634	-13.2975
400	4.5905	4.3925	31.3689	26.9764	39.0610	35.7222	-10.3406
500	4.6188	4.4350	32.3964	27.9614	32.1697	28.0037	-7.2671
600	4.6455	4.4679	33.2408	28.7730	27.5802	22.8898	-5.2585
700	4.6715	4.4951	33.9589	29.4638	24.3056	19.2558	-3.8510
800	4.6972	4.5188	34.5844	30.0656	21.8530	16.5393	-2.8149
900	4.7226	4.5400	35.1391	30.5991	19.9482	14.4277	-2.0239
1000	4.7479	4.5595	35.6380	31.0785	18.4269	12.7337	-1.4031
1030.90	4.7557	4.5653	35.7826	31.2173	18.0170	12.2749	-1.2379
1100	4.7730	4.5778	36.0917	31.5139	17.1845	11.3381	-.9053
1200	4.7982	4.5951	36.5081	31.9130	16.1513	10.1612	-.4994
1300	4.8233	4.6117	36.8931	32.2814	15.2789	9.1481	-.1639
1400	4.8483	4.6277	37.2515	32.6238	14.5330	8.2594	.1161
1500	4.8734	4.6432	37.5868	32.9436	13.8882	7.4664	.3516
1600	4.8984	4.6584	37.9021	33.2437	13.3255	6.7473	.5507
1700	4.9234	4.6733	38.1999	33.5266	12.8305	6.0856	.7197
1800	4.9484	4.6878	38.4820	33.7941	12.3919	5.4686	.8631
1900	4.9733	4.7022	38.7502	34.0480	12.0008	4.8860	.9846
2000	4.9983	4.7164	39.0059	34.2895	11.6501	4.3297	1.0873
2100	5.0233	4.7304	39.2504	34.5200	11.3339	3.7931	1.1734
2200	5.0482	4.7443	39.4847	34.7404	11.0476	-----	-----
2300	5.0732	4.7580	39.7096	34.9516	10.7873	-----	-----
2400	5.0982	4.7717	39.9260	35.1543	10.5498	-----	-----
2500	5.1231	4.7853	40.1347	35.3494	10.3322	-----	-----

^aThe reference element is crystal potassium below 336.35^o K and liquid potassium above 336.35^o K.

Liquid

The following equations for the thermodynamic properties of the liquid in the range of 338^o to 1070^o K were taken from reference 13:

$$\left(H_T^o\right)_l - \left(H_0^o\right)_c = -231.40909 + 8.8849061 T - 2.2831074 \times 10^{-3} T^2 + 9.792447 \times 10^{-7} T^3 \quad (1)$$

$$\left(C_p^o\right)_l = 8.8849061 - 4.5662147 \times 10^{-3} T + 2.9377334 \times 10^{-6} T^2 \quad (2)$$

$$\left(S_T^o\right)_l = 20.458252 \log T - 4.5662147 \times 10^{-3} T + 1.4688667 \times 10^{-6} T^2 - 32.310079 \quad (3)$$

The units for heat capacity and entropy are calories per mole per ^oK (4.184 J/(mole)(^oK)). Equation (1) agrees well with measurements from 1040^o to 1329^o K (refs. 2 to 4).

Monomer and Dimer (Ideal Gases)

The methods used to compute the thermodynamic properties of the ideal monomer and the ideal dimer are the methods for monatomic and diatomic molecules described in reference 14. The energy levels for atomic potassium were taken from reference 15.

The molecular constants for the dimer were taken from reference 16 and are shown in table IV. The chemical energy of the monomer in its standard state $\left(H_0^o\right)_{\text{monomer}}$ can

TABLE IV. - MOLECULAR CONSTANTS^a FOR DIATOMIC POTASSIUM

Molecular weight, g/mole	78.204
Symmetry number	2
Electronic state	1Σ
Statistical weight	1
Zero-order vibrational frequency, ω_e , cm^{-1}	92.64
Anharmonicity constant, $\omega_e x_e$, cm^{-1}	0.354
Rotational constant, B_e , cm^{-1}	0.05622
Vibration-rotation interaction constant, α_e , cm^{-1}	0.000219
Spectroscopic constant for rotational stretching, D_e , cm^{-1}	8.34×10^{-8}

^aConstants from Herzberg (ref. 16).

be computed from the relation

$$\left(\text{H}_0^{\text{O}}\right)_{\text{monomer}} = \left(\text{H}_0^{\text{O}}\right)_{\text{c}} - \left(\Delta\text{H}_{298}^{\text{O}}\right)_{\text{v}} + \Delta\left(\text{H}_{298}^{\text{O}} - \text{H}_0^{\text{O}}\right)_{\text{v}} = 19\,703.3 \text{ cal/mole (82\,438.6 J/mole)}$$

where

$$\Delta\left(\text{H}_{298}^{\text{O}} - \text{H}_0^{\text{O}}\right)_{\text{v}} = \left(\text{H}_{298}^{\text{O}} - \text{H}_0^{\text{O}}\right)_{\text{monomer}} - \left(\text{H}_{298}^{\text{O}} - \text{H}_0^{\text{O}}\right)_{\text{c}}$$

The chemical energy of the crystal in its standard state $\left(\text{H}_0^{\text{O}}\right)_{\text{c}}$ has been shown to equal -1693.0 calories per mole (-7083.5 J/mole). The average value of $\left(\Delta\text{H}_{298}^{\text{O}}\right)_{\text{v}}$ is 21 184.6 calories per mole (88 636.4 J/mole) from table V. This value is the average of the apparent values resulting from the thermodynamic analysis presented herein.

TABLE V. - APPARENT VALUES OF
ENTHALPY CHANGE ON EQUILIBRIUM
VAPORIZATION TO 1 MOLE OF REAL
MONOMER AT 298.15° K AS FUNC-
TION OF TEMPERATURE

Temperature, T, °K	Apparent values ^a of $\left(\Delta\text{H}_{298}^{\text{O}}\right)_{\text{v}}$	
	cal/mole	J/mole
900	21 256.2	88 935.9
950	21 239.0	88 864.0
1000	21 223.0	88 797.0
1030.9	21 213.6	88 757.7
1100	21 194.1	88 676.1
1150	21 181.0	88 621.3
1200	21 168.6	88 569.4
1250	21 156.7	88 519.6
1300	21 144.9	88 470.3
1350	21 132.9	88 420.1
1400	21 120.5	88 368.2

^aAverage $\left(\Delta\text{H}_{298}^{\text{O}}\right)_{\text{v}} = 21\,184.6 \text{ cal/mole};$

$= 88\,636.4 \text{ J/mole}$

Spread = 136 cal (569 J)

= 0.65 percent

From reference 17,

$$(\Delta H_0^{\circ})_{\text{dimer}} = -D_0^{\circ} = (H_0^{\circ})_{\text{dimer}} - 2(H_0^{\circ})_{\text{monomer}} = -11\,850 \text{ cal/mole}; -49\,580 \text{ J/mole}$$

Therefore,

$$(H_0^{\circ})_{\text{dimer}} = -11\,850 + 2(19\,703.3) = 27\,556.6 \text{ cal/mole}; 115\,296.8 \text{ J/mole}$$

Heats of Formation and Equilibrium Constants

Values for heats of formation of the ideal species from K (crystal and liquid) (i. e., $(\Delta H_T^{\circ})_f$) are given in tables I to III. For K_2 (ideal gas) at 298.15° K, for example,

$$(\Delta H_{298.15}^{\circ})_{f, \text{dimer}} = (H_{298.15}^{\circ})_{\text{dimer}} - 2(H_{298.15}^{\circ})_c$$

The logarithms of the equilibrium constants for the type of reaction just discussed are also listed in tables I to III. The equilibrium constant \mathcal{K}_f for formation from the assigned reference element is obtained from the standard free-energy change $(\Delta F_T^{\circ})_f$, for example,

$$(\Delta F_T^{\circ})_{f, \text{dimer}} = (F_T^{\circ})_{\text{dimer}} - 2(F_T^{\circ})_{\text{cond}}$$

by the following equation:

$$\log \mathcal{K}_f = -\frac{(\Delta F_T^{\circ})_f}{2.3025851 RT} \quad (4)$$

Physical Constants

The atomic weight, 39.102 grams per mole, was taken from Cameron and Wichers (ref. 18). The values of the universal gas constant R , 1.98717 calories per mole per $^{\circ}\text{K}$ (8.3143 J/(mole)($^{\circ}\text{K}$), the entropy constant, -3.664953, and the second radiation constant

hc/k, 1.43879 were computed from the constants given in reference 19.

SELECTION OF REAL-GAS DATA

The initial data considered in the thermodynamic analysis are vapor pressures, second virial coefficients, heat of dissociation of dimer at 0° K, heats of vaporization, and volumes of vapor. Where it is appropriate, the manner of selecting these data is discussed in the following paragraphs.

Vapor Pressures

References 2 to 4 present vapor pressures measured with great care from 1127° to 1575° K. Several sets of data in the range from 372° to 2078° K are also available. Each set was combined with the data of references 2 to 4 and fitted by the least-squares technique to a three-constant equation. Four of the sets did not increase the standard deviation of the data of references 2 to 4 appreciably. Therefore, these four sets (refs. 9 to 11 and Bowles' data) were pooled with the data of references 2 to 4 and yielded an overall standard deviation of 1.43 percent.

The data of reference 20 were not used because of the uncertain corrections made to the raw data. The data of Buck and Pauly (ref. 21) and of Rigney et al. (ref. 22) are considered acceptable but were not available when the analysis was completed.

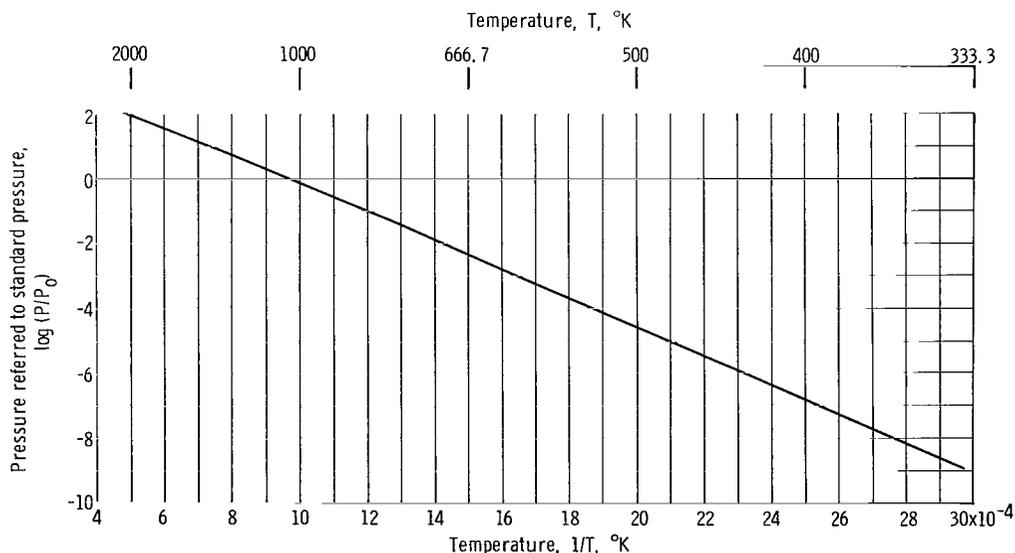


Figure 1. - Smoothed experimental vapor pressures above liquid potassium (336.35° to 2100° K).

TABLE VI. - BOILING POINTS OF POTASSIUM FROM
 10^{-8} TO 10^2 UNITS OF PRESSURE REFERRED TO
 STANDARD PRESSURE

Pressure, $\log(P/P_0)$	Boiling points, ^a °K	Pressure, $\log(P/P_0)$	Boiling points, ^a °K
-8	361.21	-2	700.36
-7	392.64	-1	833.18
-6	430.17	0	1030.90
-5	475.78	1	1359.35
-4	532.41	2	2027.78
-3	604.71		

^aFrom eq. (5) $\log\left(\frac{P}{P_0}\right) = -\frac{4625.63}{T} + 6.59817 - 0.700643 \log T$.

The equation fitted to the accepted vapor pressures referred to the standard pressure P_0 of 1 atmosphere ($1.01325 \times 10^5 \text{ N/m}^2$) is

$$\log\left(\frac{P}{P_0}\right) = -\frac{4625.3}{T} + 6.59817 - 0.700643 \log T \quad (5)$$

Figure 1 and table VI present the smoothed experimental vapor pressures of liquid potassium from this equation as a function of the boiling points.

Heat of Dissociation of Dimer at 0° K and Second Virial Coefficients

The heat of dissociation of the dimer D_0^0 at 0° K and the second virial coefficients can be related by the following expressions

$$-B = RT \mathcal{H}_{\text{dimerization}} \quad (\text{ref. 6})$$

$$\left(\Delta F_T^0\right)_{\text{dimerization}} = -RT \ln \mathcal{H}_{\text{dimerization}} \quad (\text{ref. 23})$$

and the identity

$$\left(\Delta F_T^0\right)_{\text{dimerization}} \equiv \Delta\left(F_T^0 - H_0^0\right)_{\text{dimerization}} - D_0^0$$

where

$$D_0^0 = -(\Delta H_0^0)_{\text{dimerization}}$$

Therefore,

$$-B = RT \exp \left[\frac{D_0^0 - \Delta(F_T^0 - H_0^0)_{\text{dimerization}}}{RT} \right] \quad (6)$$

Equation (6) was used to calculate values of the second virial coefficient B from $D_0^0 = 11\,850$ calories per mole (49 580 J/mole) (ref. 17) and values of $F_0^0 - H_0^0$ for the ideal monomer and dimer. These values of B may be compared with the two latest sets in the literature, those from Davies et al. (ref. 6) and those from Ewing et al. (ref. 2 to 4).

Davies et al. calculated values of B from two estimates of the potential energy curve for the interaction of ground-state K atoms, one from the Rydberg potential¹ and the other from an adjusted Rydberg potential. Ewing et al. obtained values of B graphically from their PVT data.

The following table shows that the values of B based on D_0^0 (B_V , cm^3/mole) seem to favor the average of Davies' two sets.

Temperature, T, °K	Second virial coefficient $-B$, cc/mole, from -				
	Eq. (6) for a dissociation energy D_0^0 of 11 850 cal/mole	Ref. 6			Ref. 2
		By Rydberg potential	By adjusted Rydberg po- tential	Average	
1100	3900	3550	4390	3970	4824
1200	2620	2320	2890	2605	3276
1300	1860	1630	2040	1835	2376
1400	1420	1250	1570	1410	1815
1500	1111	960	1210	1085	1443
1600	906	770	990	880	1186

¹The Rydberg potential is "the most realistic three-parameter diatomic potential energy function that is available at present" (ref. 24). It uses spectroscopic values of D_0^0 , equilibrium internuclear separations, and vibrational frequencies.

Therefore, a curve fit of the average values of B was used in the analysis. The equation selected was of the following form:

$$\log(-B) = \frac{a}{T} + b + c \log T \quad (7)$$

The method of least squares yielded the constants

$$a = 2943.72$$

$$b = -2.52548$$

$$c = 1.13330$$

Heat of Vaporization of Liquid and Volume of Vapor

Achener (ref. 9) reported direct measurements of the heat of vaporization of liquid potassium in the range 815° to 1315° K. Ewing et al. (refs. 2 to 4) have measured the volumes of the saturated vapor in the range 1127° to 1575° K.

DEVELOPMENT OF VIRIAL EQUATION OF STATE

If it is assumed that potassium vapor exists as an ideal monomer, it can be shown that third-law heats of vaporization at some reference temperature vary appreciably with the temperature at which the vapor pressure was measured. For example, substituting the fitted vapor pressures from equation (5) and the values for sensible free-energy changes for vaporization to the ideal monomer into the third-law expression

$$\left(\Delta H_{298}^{\circ}\right)_v = -RT \ln P - \Delta\left(F_T^{\circ} - H_{298}^{\circ}\right)_v$$

yields heats of vaporization of 20 850, 20 557, 20 010, and 19 146 calories per mole (87 236, 86 010, 83 722, and 80 107 J/mole) at 500° , 1000° , 1500° , and 2000° K, respectively. This nonideality can be explained by assuming either that the vapor consists of more than one molecular species or that it is a monatomic imperfect gas.

Preliminary analysis in terms of an ideal mixture of monomer and dimer did not correlate the experimental vapor pressures satisfactorily. Since the properties of the

higher polymers of potassium are not known, the mixture approach was not pursued any further. Therefore, the vapor was treated as an imperfect gas.

Formulation of Third and Fourth Virial Coefficients

The virial equation of state, to the number of terms used in the present work,

$$PV = RT + BP + CP^2 + DP^3 \quad (8)$$

describes the deviations from ideality in terms of the virial coefficients B , C , and D , which are functions of T .

It is necessary to express B , C , and D as explicit functions of T in order to use the equation of state (eq. (8)) directly. Unfortunately, an explicit function based on a realistic potential (ref. 6) is available only for B (i. e., eq. (7)). One way to overcome this difficulty is to assume relations of the following type:

$$C = \frac{d_1(-B)^m}{T^n} \quad (9a)$$

$$D = \frac{d_2(-B)^q}{T^r} \quad (9b)$$

and to substitute these relations into equation (8). Then the constants d_1 , d_2 , m , n , q , and r could be fitted to the PVT data (refs. 2 to 4).

The preceding empirical approach was improved by deriving values of m , n , q , and r from two less realistic potentials, the Lennard-Jones 12-6 (ref. 7) and the hard-sphere (ref. 8) potentials.

In this way, only the scale factors d_1 and d_2 were fitted to the PVT data. The set of constants derived from the Lennard-Jones potential is $m = 8.5561$, $n = -10.056$, $q = 12.359$, and $r = -13.093$. For the hard-sphere potential, the constants are $m = 2$, $n = 1$, $q = 3$, and $r = 2$. For this potential, equations (9a) and (9b) simplify to

$$C = \frac{k_1 B^2}{T} \quad (10a)$$

$$D = \frac{k_2 B^3}{T^2} \quad (10b)$$

The hard-sphere relation reproduces the experimental volumes (refs. 2 to 4) somewhat better than the Lennard-Jones relation (0.75 percent standard deviation against 2.20 percent). Either potential provides a good representation of the experimental heats of vaporization (ref. 9) (3.11 percent standard deviation against 3.25 percent).

Table VII compares the two models with respect to fugacity-pressure ratio f/P , heat capacity C_p , and isentropic expansion index γ_s . Figure 2 shows the variation in C_p . From 1000° to 2000° K, either potential yields a gradual variation for f/P , C_p , and γ_s . However, between 800° and 1000° K, the Lennard-Jones potential shows a sharp decrease in C_p and a sharp increase in γ_s .

TABLE VII. - COMPARISON OF THERMODYNAMIC PROPERTIES FROM LENNARD-JONES 12-6 AND HARD-SPHERE POTENTIALS

Temperature, T, °K	Lennard-Jones potential				Hard-sphere potential			
	Fugacity- pressure ratio, f/P	Real-gas heat capacity at constant pressure, C_p		Isentropic expansion index, γ_s , $\left(\frac{\partial \ln P}{\partial \ln \rho}\right)_s$	Fugacity- pressure ratio, f/P	Real-gas heat capacity at constant pressure, C_p		Isentropic expansion index, γ_s , $\left(\frac{\partial \ln P}{\partial \ln \rho}\right)_s$
		cal (mole)(°K)	J (mole)(°K)			cal (mole)(°K)	J (mole)(°K)	
336.35	-----	-----	-----	-----	0.99995	5.012	20.970	1.659
500	-----	-----	-----	-----	.9982	5.627	23.543	1.583
800	0.9307	39.37	164.72	1.095	.9744	8.679	36.313	1.448
900	.9564	21.70	90.79	1.201	.9590	9.748	40.786	1.437
1000	.9418	11.36	47.53	1.392	.9408	10.671	44.647	1.434
1500	.8420	11.59	48.49	1.451	.8336	12.311	51.509	1.440
2000	.7569	10.96	45.86	1.389	.7423	10.683	44.698	1.371

On the other hand, the hard-sphere relation shows a gradual variation in all three properties over the entire range of temperatures. Therefore, the hard-sphere relation probably gives a better description of the properties of potassium vapor.

This conclusion does not imply that potassium is a hard-sphere gas. It may indicate that, when the Rydberg potential curves for higher interactions are eventually determined, the expressions for C and D will show dependencies on B which are similar to those for a hard-sphere gas.

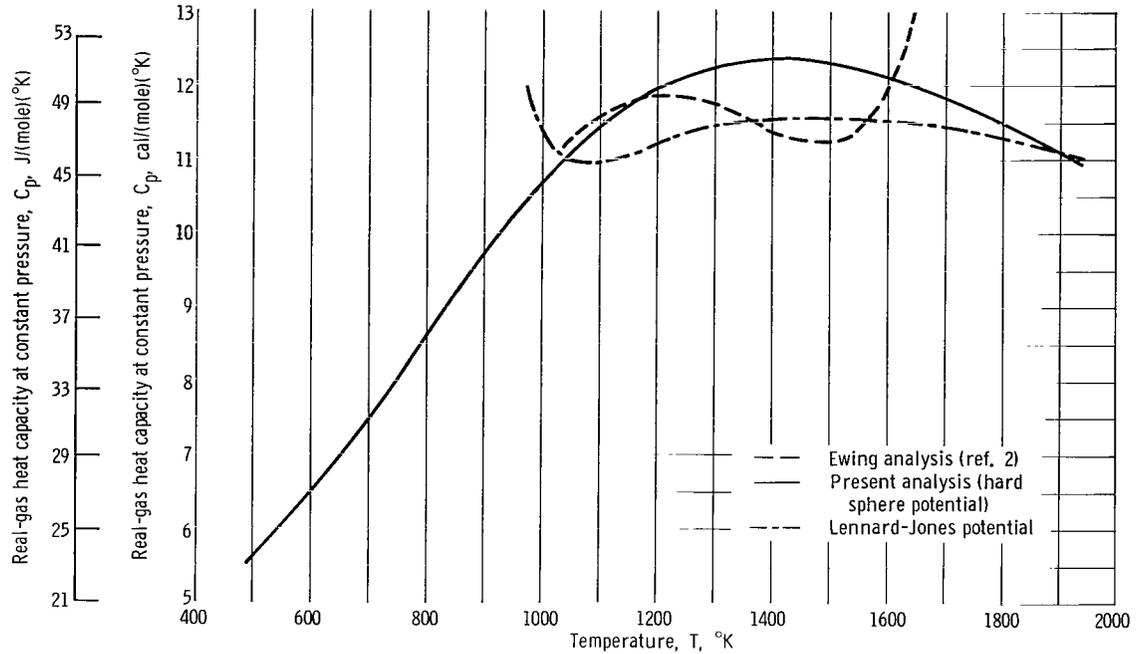


Figure 2. - Comparison of calculated heat capacities of saturated vapor.

Hard-Sphere Expressions Used for Higher Virial Coefficients

Equation (7) derived from Davies' second virial coefficients can be expressed as

$$B_V = -10^b 10^{a/T} T^c \text{ cm}^3/\text{mole} \quad (11)$$

Expressing B in calories per mole per atmosphere ($4.12929 \times 10^{-5} \text{ J}/(\text{mole})(\text{N}/\text{m}^2)$) yields

$$B = c_1 10^{a/T} T^c \quad (11a)$$

where

$$c_1 = -0.024217256 \times 10^b$$

Substituting equations (10) into equation (8) results in

$$PV = RT + BP + k_1 \frac{B^2 P^2}{T} + k_2 \frac{B^3 P^3}{T^2} \quad (12)$$

Further substitution of equation (11a) into equation (12) yields

$$PV = RT + c_1 10^{a/T} T^c P + c_2 10^{2a/T} T^{2c-1} P^2 + c_3 10^{3a/T} T^{3c-2} P^3 \quad (13)$$

where

$$c_2 = k_1 c_1^2 \quad (14a)$$

$$c_3 = k_2 c_1^3 \quad (14b)$$

With the values of a , b , and c (and therefore c_1) determined from Davies' second virial coefficients, the constants c_2 and c_3 were fitted to the PVT data. The curve-fitting process yielded

$$c_2 = -2.55216 \times 10^{-9}$$

and

$$c_3 = 2.41943 \times 10^{-13}$$

Fitting equation (8) yields

$$c_1 = -7.22185 \times 10^{-5}$$

Therefore,

$$k_1 = -0.489340$$

and

$$k_2 = -0.642345$$

Thus, the final recommended equation of state becomes

$$PV = RT - 7.22185 \times 10^{-5} 10^{2943.72/T} T^{1.13330} P - 2.55216 \times 10^{-9} 10^{5887.44/T} T^{1.26660} P^2 + 2.41943 \times 10^{-13} 10^{8831.16/T} T^{1.39990} P^3 \quad (15)$$

Consistency Test for Equation of State

It is necessary to calculate the heat of vaporization at 298.15° K as a function of temperature in order to check the consistency of the calculated properties from equation (15).

The basic equation for a real gas obeying equation (8) is

$$(F - F^0)_T = RT \ln P + BP + \frac{CP^2}{2} + \frac{DP^3}{3} \quad (16)$$

which is derived in appendix B. The relative free energy $(F - F^0)_T$ is the constant-temperature free energy of the real gas relative to the free energy of the ideal gas.

The quantity Q , defined in reference 5 as

$$Q \equiv -\Delta(F_T^0 - H_{298}^0)_v - RT \ln P \quad (17)$$

can be simply related to the virial coefficients in the following manner. The ideal free energy of vaporization is defined as

$$(\Delta F_T^0)_v \equiv (F_T^0)_{\text{monomer}} - (F_T^0)_{\text{cond}} \quad (18)$$

On the saturation line, equilibrium demands

$$(F_T)_{\text{monomer}} = (F_T)_{\text{cond}} \quad (19)$$

If it is assumed that the condensed phase is in its standard state,

$$(F_T)_{\text{monomer}} = (F_T^0)_{\text{cond}} \quad (20)$$

Substituting equation (20) into equation (18) yields

$$\left(\Delta F_T^0\right)_v = (F^0 - F)_{T, \text{ monomer}} \quad (21)$$

and substituting equation (21) into equation (17) yields

$$Q = (F - F^0)_{T, \text{ monomer}} - RT \ln P + \left(\Delta H_{298}^0\right)_v \quad (22)$$

Substituting equation (16) into equation (22) gives

$$\left(\Delta H_{298}^0\right)_v = Q - BP - \frac{CP^2}{2} - \frac{DP^3}{3} \quad (23)$$

Using equations (10) results in

$$\left(\Delta H_{298}^0\right)_v = Q - BP - \frac{k_1}{2} \frac{B^2 P^2}{T} - \frac{k_2}{3} \frac{B^3 P^3}{T^2} \quad (24)$$

Since k_1 and k_2 have already been determined by fitting the PVT data (1127^o to 1575^o K) to equation (12), it is a simple matter to compute apparent values of $\left(\Delta H_{298}^0\right)_v$.

The choice of a reasonable interval for averaging $\left(\Delta H_{298}^0\right)_v$ must be a compromise because there is only a small interval (1100^o to 1300^o K) that includes experimental values of both the vapor volume and the heat capacity of the liquid. A representative average probably could be obtained by a small extrapolation of volumes to 900^o K (i. e., using eq. (13)) and a small extrapolation of the cubic equation for heat capacity (eq. (2)) to 1400^o K. The interval from 900^o to 1400^o K was thus chosen for averaging $\left(\Delta H_{298}^0\right)_v$. In this way, from 900^o to 1100^o K, experimental enthalpies were combined with extrapolated volumes, and, from 1300^o to 1400^o K, extrapolated enthalpies were combined with experimental volumes.

Table V shows the variation in apparent values of $\left(\Delta H_{298}^0\right)_v$ as a function of temperature. The maximum difference is 0.65 percent, with an average value of 21 184.6 calories per mole (88 636.4 J/mole).

REAL-GAS PROPERTIES ON SATURATION LINE

Table VIII presents calculated real-gas properties on the saturation line at assigned

TABLE VIII. - THERMODYNAMIC PROPERTIES OF REAL MONOMER GAS ON SATURATION LINE

Temperature, T, °K	Pressure referred to standard pressure, P/P ₀	Volume, cm ³ /mole	Real-gas heat capacity at constant pressure (gas phase), C _p (g)/R	Enthalpy (crystal phase), H _T ⁰ (c) / RT	Enthalpy change on equilibrium vaporization to 1 mole of real monomer at T °K, (H _T) _v / RT	Enthalpy of real gas at T °K (gas phase), H _T (g) / RT	Entropy for standard state (crystal phase), S _T ⁰ (c)/R	Entropy change on equilibrium vaporization to 1 mole of real monomer at T °K, (ΔS _T) _v / R	Entropy of real gas at T °K (gas phase), S _T (g) / R	Isentropic expansion index, γ _s
^a 336.35	1.18949×10 ⁻⁹	2.32015×10 ¹³	2.5219	1.2612	31.0561	32.3174	9.0651	31.0561	32.3174	1.6592
400.00	1.62548×10 ⁻⁷	2.01864×10 ¹¹	2.5850	1.6694	25.9050	27.5744	9.7284	25.9050	27.5744	1.6403
500.00	2.85692×10 ⁻⁵	1.43345×10 ⁹	2.8315	2.0830	20.4411	22.5242	10.5629	20.4411	22.5242	1.5832
600.00	8.75583×10 ⁻⁴	5.58893×10 ⁷	3.2585	2.3452	16.7689	19.1141	11.2296	16.7689	19.1141	1.5198
700.00	9.92504×10 ⁻³	5.70606×10 ⁶	3.7976	2.5249	14.1122	16.6371	11.7851	14.1122	16.6371	1.4741
800.00	6.05489×10 ⁻²	1.05570×10 ⁶	4.3676	2.6569	12.0866	14.7435	12.2633	12.0866	14.7435	1.4483
900.00	2.44746×10 ⁻¹	2.88902×10 ⁵	4.9055	2.7602	10.4818	13.2420	12.6858	10.4818	13.2420	1.4368
1000.00	7.42360×10 ⁻¹	1.03634×10 ⁵	5.3699	2.8466	9.1731	12.0196	13.0675	9.1731	12.0196	1.4341
^b 1030.90	1.00001×10 ⁰	7.87392×10 ⁴	5.4945	2.8710	8.8155	11.6865	13.1789	8.8155	11.6865	1.4343
1100.00	1.82863×10 ⁰	4.51586×10 ⁴	5.7376	2.9232	8.0817	11.0050	13.4191	8.0817	11.0050	1.4358
1200.00	3.85545×10 ⁰	2.27353×10 ⁴	5.9992	2.9950	7.1554	10.1504	13.7483	7.1554	10.1504	1.4390
1300.00	7.21497×10 ⁰	1.27796×10 ⁴	6.1561	3.0654	6.3572	9.4226	14.0612	6.3572	9.4226	1.4416
1400.00	1.22982×10 ¹	7.82923×10 ³	6.2171	3.1368	5.6605	8.7973	14.3624	5.6605	8.7973	1.4421
1500.00	1.94587×10 ¹	5.13751×10 ³	6.1954	3.2109	5.0450	8.2559	14.6554	5.0450	8.2559	1.4396
1600.00	2.89875×10 ¹	3.56476×10 ³	6.1065	3.2891	4.4949	7.7840	14.9433	4.4949	7.7840	1.4334
1700.00	4.10983×10 ¹	2.59021×10 ³	5.9662	3.3725	3.9975	7.3700	15.2286	3.9975	7.3700	1.4233
1800.00	5.59237×10 ¹	1.95624×10 ³	5.7893	3.4617	3.5427	7.0043	15.5130	3.5427	7.0043	1.4094
1900.00	7.35185×10 ¹	1.52666×10 ³	5.5888	3.5574	3.1219	6.6793	15.7985	3.1219	6.6793	1.3919
2000.00	9.38677×10 ¹	1.22537×10 ³	5.3761	3.6602	2.7282	6.3884	16.0863	2.7282	6.3884	1.3713
2100.00	1.16897×10 ²	1.00773×10 ³	5.1603	3.7704	2.3557	6.1262	16.3777	2.3557	6.1262	1.3482

Temperature, T, °K	Fugacity-pressure ratio, f/P	Second virial coefficient, B _v , cm ³ /mole	Third virial coefficient, C _v , (cm ³ /mole) ²	Fourth virial coefficient, D _v , (cm ³ /mole) ³	Compressibility factor, Z	Density, g/cc	Volume-temperature coefficient, (∂v/∂T) _P , cm ³ /(mole)(°K)	Volume-pressure coefficient, (∂v/∂(P/P ₀)) _T , cm ³ /mole
^a 336.35	0.999947	-1.230535×10 ⁹	-5.928597×10 ¹⁹	8.281390×10 ³⁰	0.999947	1.685319×10 ⁻¹²	1.672289×10 ⁹	-4.723930×10 ²⁰
400.00	.999700	-6.063725×10 ⁹	-1.439605×10 ¹⁷	9.909236×10 ²⁶	.999700	1.937050×10 ⁻¹⁰	1.228322×10 ⁷	-3.008377×10 ¹⁶
500.00	.998166	-2.634548×10 ⁶	-2.717544×10 ¹⁴	8.127188×10 ²²	.998162	2.727819×10 ⁻⁸	7.114748×10 ⁴	-1.217337×10 ¹²
600.00	.993986	-3.382215×10 ⁵	-4.478853×10 ¹²	1.719593×10 ²⁰	.993950	6.996327×10 ⁻⁷	2.409950×10 ³	-1.555273×10 ⁹
700.00	.986148	-8.020207×10 ⁴	-2.518463×10 ¹¹	2.292867×10 ¹⁸	.985962	6.852720×10 ⁻⁶	2.245802×10 ²	-1.412355×10 ⁷
800.00	.974375	-2.781269×10 ⁴	-3.028659×10 ¹⁰	9.562052×10 ¹⁶	.973749	3.703889×10 ⁻⁵	3.929410×10 ¹	-4.338637×10 ⁵
900.00	.959012	-1.239835×10 ³	-6.018550×10 ⁹	8.470583×10 ¹⁵	.957445	1.353467×10 ⁻⁴	1.040741×10 ¹	-2.989555×10 ⁴
1000.00	.940765	-6.578704×10 ³	-1.694513×10 ⁹	1.265444×10 ¹⁵	.937573	3.773103×10 ⁻⁴	3.662369×10 ⁰	-3.614396×10 ³
^b 1030.90	.934673	-5.557559×10 ³	-1.209296×10 ⁹	7.629116×10 ¹⁴	.930823	4.966012×10 ⁻⁴	2.770519×10 ⁰	-2.054201×10 ³
1100.00	.920472	-3.957669×10 ³	-6.132582×10 ⁸	2.755120×10 ¹⁴	.914877	8.658820×10 ⁻⁴	1.575692×10 ⁰	-6.560752×10 ²
1200.00	.898953	-2.613701×10 ³	-2.674707×10 ⁸	7.935782×10 ¹³	.890196	1.719878×10 ⁻³	7.844476×10 ⁻¹	-1.611839×10 ²
1300.00	.876931	-1.853325×10 ³	-1.344830×10 ⁸	2.829285×10 ¹³	.864364	3.059732×10 ⁻³	4.352644×10 ⁻¹	-4.988836×10 ¹
1400.00	.854994	-1.388940×10 ³	-7.553203×10 ⁷	1.190892×10 ¹³	.838149	4.994362×10 ⁻³	2.622304×10 ⁻¹	-1.848296×10 ¹
1500.00	.833588	-1.087586×10 ³	-4.631175×10 ⁷	5.717580×10 ¹²	.812206	7.611078×10 ⁻³	1.683745×10 ⁻¹	-7.895512×10 ⁰
1600.00	.813034	-8.822125×10 ²	-3.047268×10 ⁷	3.051699×10 ¹²	.787068	1.096903×10 ⁻²	1.136799×10 ⁻¹	-3.781573×10 ⁰
1700.00	.793541	-7.365236×10 ²	-2.123917×10 ⁷	1.775751×10 ¹²	.763134	1.509605×10 ⁻²	7.990948×10 ⁻²	-1.987930×10 ⁰
1800.00	.775232	-6.296788×10 ²	-1.552396×10 ⁷	1.109633×10 ¹²	.740688	1.998837×10 ⁻²	5.804938×10 ⁻²	-1.128295×10 ⁰
1900.00	.758165	-5.491063×10 ²	-1.180530×10 ⁷	7.358534×10 ¹¹	.719906	2.561276×10 ⁻²	4.333468×10 ⁻²	-6.825667×10 ⁻¹
2000.00	.742348	-4.868956×10 ²	-9.281880×10 ⁶	5.130144×10 ¹¹	.700879	3.191038×10 ⁻²	3.310014×10 ⁻²	-4.356520×10 ⁻¹
2100.00	.727753	-4.378860×10 ²	-7.507345×10 ⁶	3.731686×10 ¹¹	.683629	3.880191×10 ⁻²	2.578182×10 ⁻²	-2.909786×10 ⁻¹

^aMelting point.

^bNormal boiling point.

temperatures from 336.35⁰ to 2100⁰ K. These values are computed by the use of equation (5) for the vapor pressures and of equation (15), the derived equation of state. Details of the calculations are given in the following paragraphs.

Virial Coefficients

The virial coefficients from equation (15) are in calories per mole per atmosphere squared $\left(4.07527 \times 10^{-10} \text{ J}/(\text{mole})(\text{N}/\text{m}^2)^2\right)$ for C and in calories per mole per cubic atmosphere $\left(4.02199 \times 10^{-15} \text{ J}/(\text{mole})(\text{N}/\text{m}^2)^3\right)$ for D. The values given in table VIII have been converted to units of $(\text{cm}^3/\text{mole})$ and $(\text{cm}^3/\text{mole})^3$, respectively, in order to conform to the usual virial equation:

$$\frac{PV}{RT} = 1 + \frac{B_V}{V} + \frac{C_V}{V^2} + \frac{D_V}{V^3}$$

The conversion is accomplished by the following equations from reference 25:

$$B = B_V$$

$$C = \frac{C_V - B_V^2}{RT}$$

$$D = \frac{D_V - 3B_V C_V + 2B_V^3}{(RT)^2}$$

Volume, Entropy, Enthalpy, and Heat Capacity

The volumes are calculated at assigned temperatures from equation (15) by use of the smoothed experimental vapor pressures. The fugacity-pressure ratio f/P is calculated from equation (B9).

The relative functions $(S - S^0)_T$, $(H - H^0)_T$, and $(C_p - C_p^0)_T$ are calculated from equations (B11), (B12), and (B13). Adding the relative functions to the corresponding functions of the ideal monomer yields the following functions for the real gas on the saturation line:

$$S_T = (S - S^0)_T + S_T^0 \quad (24a)$$

$$H_T = (H - H^0)_T + H_T^0 \quad (24b)$$

$$C_p = (C_p - C_p^0)_T + C_p^0 \quad (24c)$$

It is necessary to calculate H_T^0 for the ideal monomer as follows, in order to compute the function H_T for the real monomer:

$$(\Delta H_{298}^0)_v = (H_{298}^0)_c - (H_{298}^0)_{\text{monomer}} = - (H_{298}^0)_{\text{monomer}}$$

Since $(H_T^0 - H_{298}^0)$ has already been calculated for the ideal monomer (table II, p. 4),

$$(H_T^0)_{\text{monomer}} = (H_T^0 - H_{298}^0)_{\text{monomer}} - (\Delta H_{298}^0)_v$$

Enthalpy of Vaporization and Entropy of Vaporization

The enthalpy of vaporization in calories per mole (4.184 J/mole) is simply

$$(\Delta H_T)_v = (H_T)_{\text{monomer}} - (H_T)_l$$

The entropy of vaporization, in calories per mole per $^{\circ}\text{K}$ (4.184 J/(mole)($^{\circ}\text{K}$)) is calculated from the expression

$$(\Delta S_T)_v = \frac{(\Delta H_T)_v}{T}$$

The use of this expression in the real-gas table implies the use of the apparent values of $(\Delta H_{298}^0)_v$. However, this use is necessary to meet the requirement of a zero Gibbs free energy change $(\Delta F_T)_v$ on the saturation line.

Density

Since the volume V of the real gas is in cubic centimeters per mole of monomer (39.102 g), the density is $\rho = 39.102/V$ in grams per cubic centimeter.

Volume-Temperature and Volume-Pressure Coefficients

The volume-temperature coefficient $(\partial V/\partial T)_P$ and the volume-pressure coefficient $(\partial V/\partial P)_T$ are needed to compute the isentropic expansion index (eq. (29)) and also the coefficients of thermal expansion and compressibility as follows (ref. 23):

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P$$

and

$$\kappa = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T$$

Solving equation (8) for V and differentiating with respect to P at constant T yield

$$V = \frac{RT}{P} + B + CP + DP^2$$

and

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} + C + 2DP \quad (25)$$

Differentiating V with respect to T at constant P results in

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT} + P \frac{dC}{dT} + P^2 \frac{dD}{dT} \quad (26)$$

Differentiating equations (10) gives

$$\frac{dC}{dT} = \frac{2C}{B} \frac{dB}{dT} - \frac{C}{T} \quad (27a)$$

$$\frac{dD}{dT} = \frac{3D}{B} \frac{dB}{dT} - \frac{2D}{T} \quad (27b)$$

Substituting equations (27) into equation (26) yields

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT} + \frac{2PC}{B} \frac{dB}{dT} + \frac{3P^2D}{B} \frac{dB}{dT} - \frac{PC}{T} - \frac{2P^2D}{T}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{d \ln B}{dT} (B + 2CP + 3DP^2) - \frac{P}{T} (C + 2PD) \quad (28)$$

Isentropic Expansion Index

The isentropic expansion index is defined (ref. 1) as

$$\gamma_s = -\frac{V}{P} \left(\frac{\partial P}{\partial V}\right)_S \quad (29)$$

where

$$\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{\left[\left(\frac{\partial V}{\partial P}\right)_T + \frac{T}{C_p} \left(\frac{\partial V}{\partial T}\right)_P^2\right]}$$

Simple substitution of T , C_p , equation (25), and equation (28) into equation (29) yields the isentropic expansion index.

COMPARISON OF CALCULATED REAL-GAS PROPERTIES WITH EXPERIMENTAL DATA AND ANOTHER ANALYSIS

The real-gas properties presented compare favorably with the experimental data and the calculated heat capacity appears to show a more reasonable trend with temperature than the result of an empirical analysis (ref. 2) as shown in the following paragraphs.

Enthalpy of Vaporization and Entropy of Vaporization

Figure 3 compares Achener's (ref. 9) experimental enthalpies of vaporization with those computed herein and those computed by Ewing (ref. 2). Figure 4 is a similar comparison for the entropies of vaporization.

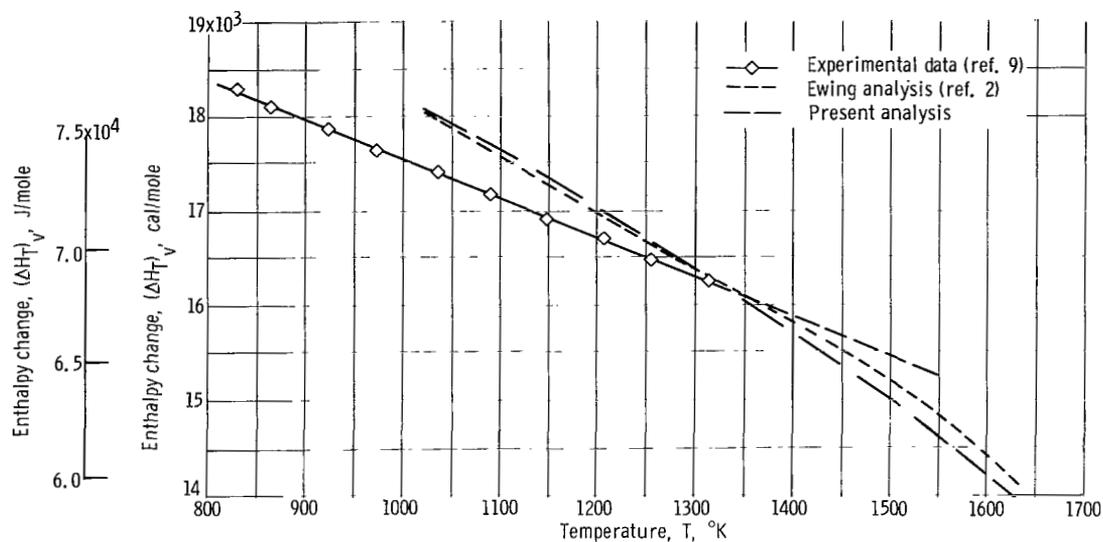


Figure 3. - Comparison of calculated and experimental heats of vaporization.

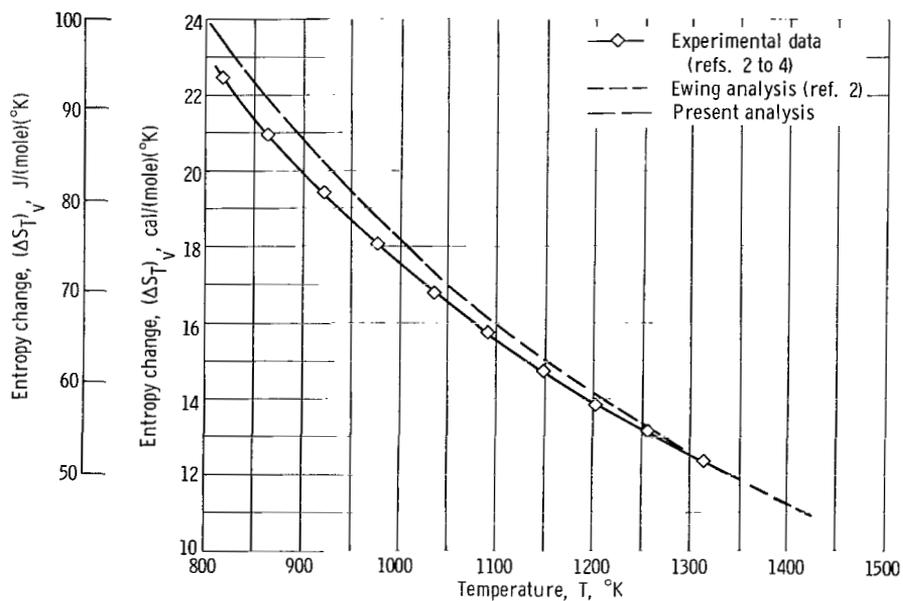


Figure 4. - Comparison of calculated and experimental entropies of vaporization.

The two sets of calculated heats of vaporization agree very well and differ from experiment by about 3.5 percent (maximum). The entropies show a similar trend.

Volume

When the choice of a potential function for the higher virial coefficients was discussed in the section DEVELOPMENT OF VIRIAL EQUATION OF STATE, the author explained that the constants k_1 and k_2 were fitted to the volumes, vapor pressures, and virial coefficients. The heats of vaporization were not fitted because their formulation not only involves the virial coefficients but also their derivatives with respect to temperature (cf eq. (B12)). It is therefore not surprising that the volumes deviated less from experiment than did the heats of vaporization (0.75 percent against 3.11 percent).

Isentropic Expansion Index

Goldman (ref. 1) reported experimental expansion indexes γ_s varying from 1.33 to 1.42 in the range from 943° to 1051° K, with an average of 1.38. From the equation of state of the present work, γ_s values of 1.434 at 1000° K and 1.436 at 1100° K were computed.

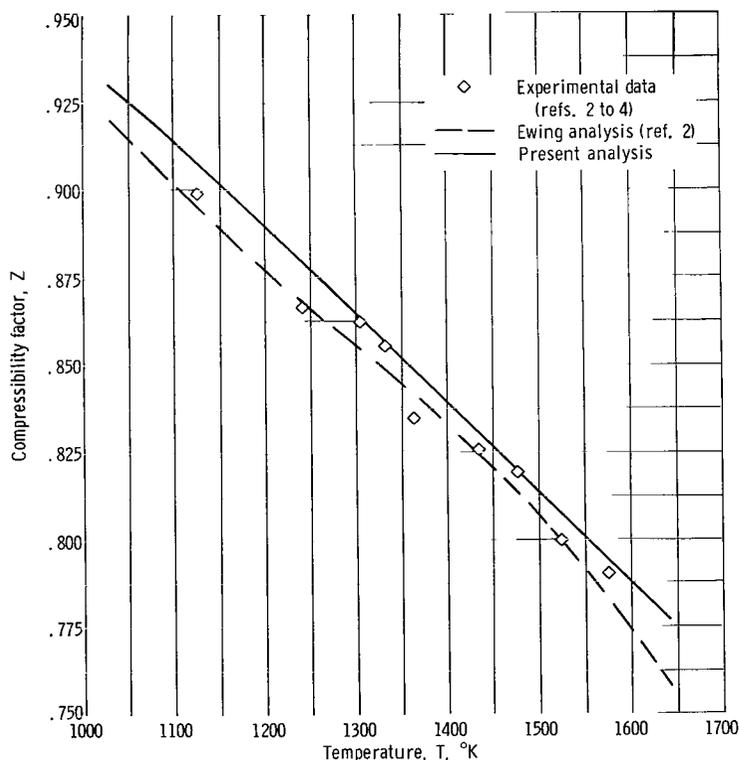


Figure 5. - Comparison of calculated and experimental compressibility factors.

Compressibility Factor

Figure 5 compares Ewing's nine experimental compressibility factors Z (ref. 2) with those computed by Ewing et al. (ref. 2) and those computed herein. Some of the experimental compressibility factors are closer to Ewing's curve, some are closer to the present curve, and a few agree well with either curve. In view of the scatter of the experimental points, neither set of calculated compressibility factors appears to be superior.

Heat Capacity

Figure 2 and table VII illustrate the agreement of the hard-sphere and Lennard-Jones models in predicting a gradual increase in C_p of the real gas from 1100^o to 1500^o K, followed by a gentle decline. On the other hand, Ewing's analysis predicts a gradual rise to 1200^o K, a gradual decline to 1500^o K, and then a sharp increase. The agreement of both potential models in this region tends to confirm a gradual change in C_p in this temperature range.

CONCLUDING REMARKS

The method of analysis used herein, fitting of pressure-volume-temperature (PVT) data, may be compared with an alternative method of Hicks in which volumes are traded off with free energies (PFT data).

The advantages of the PVT fit are that it preserves the experimental vapor pressures and the properties of the liquid (specific heat, enthalpy, entropy, and Gibbs free energy), and only slightly perturbs the experimental volumes. The disadvantage of this approach is that it does not guarantee a temperature-independent value of enthalpy change on equilibrium vaporization to 1 mole of real monomer at 298^o K $(\Delta H_{298}^0)_v$ (eq. (23)). However, this variation in $(\Delta H_{298}^0)_v$ is small compared with the variation obtained by assuming ideal behavior. For example, between 1000^o and 1400^o K, $(\Delta H_{298}^0)_v$ for the ideal gas varies from 20 557 to 20 119 calories per mole (86 010 to 84 178 J/mole), whereas for the real gas, it varies from 21 223 to 21 120 calories per mole (88 797 to 88 366 J/mole). The variation has thus been reduced by 75 percent.

The method of Hicks for fitting pressure, free energy, and temperature does yield a constant $(\Delta H_{298}^0)_v$, but applying it to the present set of initial data caused a 9.5-percent deviation in volume and approximately a 15-percent deviation in vapor pressures below 800^o K. On the whole, therefore, the PVT fit does a better job than the PFT fit.

The variation of apparent $(\Delta H_{298}^0)_v$ obtained through this analysis at temperatures from 1127^o to 1575^o K may be caused by

1. Truncation of the virial expansion at the fourth coefficient
2. Assumption that the higher coefficients are simple functions of the second virial coefficient.
3. Discrepancies in the experimental data.

The third and fourth virial coefficients of the present analysis depart markedly from hard-sphere behavior (ref. 7) in two ways: First, the scale factors differ as follows:

Fit to PVT data (present work):

$$C_V = 0.0276 B_V^2$$

$$D_V = -4.454 B_V^3$$

Theoretical hard-sphere model:

$$C_V = 0.625 B_V^2$$

$$D_V = 0.2869 B_V^3$$

where B_V , C_V , and D_V are the second, third, and fourth virial coefficients, respectively. Second, and of more importance, in the hard-sphere model the virial coefficients are independent of temperature, whereas C_V and D_V of the present analysis depend strongly on temperature. This dependence is caused by the fact that B is a function of temperature (eq. (7)).

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 16, 1967,
129-01-02-01-22.

APPENDIX A

SYMBOLS

a	constant	D_V	fourth virial coefficient, (cm^3/mole) ³
B	second virial coefficient, cal/(mole)(atm); J/(mole)(N/m ²)	d	constant
B_e	rotational constant, cm^{-1}	F	Gibbs free energy
B_V	second virial coefficient, cm^3/mole	F_T	Gibbs free energy of real gas at $T^\circ \text{K}$, cal/mole; J/mole
b	constant	$(F_T^\circ - H_0^\circ)$	sensible free energy for standard state at $T^\circ \text{K}$, cal/mole; J/mole
C	third virial coefficient, cal/(mole)(atm) ² ; J/(mole)(N/m ²) ²	F_0	Gibbs free energy at 0°K , cal/mole; J/mole
C_p	real-gas heat capacity at constant pressure, cal/(mole)($^\circ\text{K}$); J/(mole)($^\circ\text{K}$)	ΔF_T°	standard free-energy change
C_p°	standard-state heat capacity at constant pressure, cal/(mole)($^\circ\text{K}$); J/(mole)($^\circ\text{K}$)	$(\Delta F_T^\circ)_v$	Gibbs free-energy change on vaporization to 1 mole of real monomer at $T^\circ \text{K}$, cal/mole; J/mole
C_V	third virial coefficient, (cm^3/mole) ²	f	fugacity, atm; N/m ²
c	constant	g	gas phase
D	fourth virial coefficient, cal/(mole)(atm) ³ ; J/(mole)(N/m ²) ³	H	enthalpy
D_e	spectroscopic constant for rotational stretching, cm^{-1}	H_T	enthalpy of real gas to $T^\circ \text{K}$, cal/mole; J/mole
D_0°	dissociation energy at 0°K , cal/mole; J/mole	H_T°	sum of standard-state sensi- ble enthalpy at $T^\circ \text{K}$ and chemical energy at 0°K for standard state, cal/mole; J/mole
		$H_T^\circ - H_0^\circ$	sensible enthalpy for stan- dard state at $T^\circ \text{K}$, cal/mole; J/mole

H_0^0	chemical energy at 0^0 K for standard state, cal/mole; J/mole	Q	$-\Delta(F_T^0 - H_{298}^0)_v - RT \ln P$, cal/mole; J/mole
ΔH_T^0	enthalpy change for formation of substance from element in atomic gas state at T^0 K, cal/mole; J/mole	q	constant
$(\Delta H_T^0)_f$	enthalpy change for formation of substance from assigned reference element at T^0 K, cal/mole; J/mole	R	universal gas constant, 1.98717 cal/(mole)(0 K), 82.05601 (cm ³)(atm)/(mole)(0 K); 8.3143 J/(mole)(0 K)
$(\Delta H_T)_v$	enthalpy change on equilibrium vaporization to 1 mole of real monomer at T^0 K, cal/mole; J/mole	r	constant
$(\Delta H_T^0)_v$	enthalpy change on equilibrium vaporization to 1 mole of ideal monomer at T^0 K, cal/mole; J/mole	S	entropy of real gas, cal/(mole)(0 K); J/(mole)(0 K)
hc/k	second radiation constant	S_T	entropy of real gas at T^0 K, cal/(mole)(0 K); J/(mole)(0 K)
\mathcal{K}	equilibrium constant for reaction of formation from element in atomic gas state	S_T^0	entropy for standard state, cal/(mole)(0 K); J/(mole)(0 K)
\mathcal{K}_f	equilibrium constant for reaction of formation from assigned reference element	$(\Delta S_T)_v$	entropy change on equilibrium vaporization to 1 mole of real monomer at T^0 K, cal/(mole)(0 K); J/(mole)(0 K)
k	Boltzmann constant	$(\Delta S_T^0)_v$	entropy change on equilibrium vaporization to 1 mole of ideal monomer at T^0 K, cal/mole; J/mole
l	liquid phase	T	absolute temperature, 0 K
m	constant	V	volume, cm ³ /mole
n	constant	Z	compressibility factor; PV/RT
P	absolute pressure, atm; N/m ²	α	coefficient of thermal expansion, (0 K) ⁻¹
P_0	standard pressure, 1 atm; 1.01325 × 10 ⁵ N/m ²	α_e	vibration-rotation interaction constant for diatomic molecule, cm ⁻¹
		γ_s	isentropic expansion index, ($\partial \ln P / \partial \ln \rho$) _s

κ	coefficient of compressibility, atm^{-1} ; $(\text{N}/\text{m}^2)^{-1}$	f	formation from assigned reference element
ρ	density of vapor, g/cm^3	l	liquid
ω_e	zero-order vibrational frequency for diatomic molecule, cm^{-1}	P	constant pressure change
ω_e^x, ω_e^y	anharmonicity constants for diatomic molecules, cm^{-1}	s	constant entropy change
Subscripts:		sat	quantity at saturation
c	crystal	T	constant temperature change
cond	condensed-phase property	v	change on equilibrium vaporization to monomer
		0	quantity at 0°K
		Superscript:	
		o	standard state

APPENDIX B

DERIVATION OF RELATIVE FUNCTIONS AND FUGACITY

Relative Free Energy, $(F - F^0)_T$

For a system of constant composition,

$$dF = V dP - S dT$$

and

$$\left(\frac{\partial F}{\partial P}\right)_T = V \quad (B1)$$

For 1 mole of ideal gas, $V = RT/P$, so that integration of equation (B1) gives

$$F = RT \ln P + F^0 \quad (B2)$$

where the integration constant F^0 depends only on the temperature and nature of the gas.

For a real gas, the fugacity f is defined by the equation

$$F = RT \ln f + F^0 \quad (B3)$$

As the actual pressure P approaches zero (i. e., as the real gas approximates ideal behavior), f/P approaches 1.

To determine f , differentiate equation (B3) and utilize equation (B1) to obtain

$$\left(\frac{\partial F}{\partial P}\right)_T = V = RT \left(\frac{\partial \ln f}{\partial P}\right)_T \quad (B4)$$

At a definite temperature,

$$RT d \ln f = V dP \quad (B5)$$

where V is the actual molar volume. For the ideal gas

$$RT \, d \ln P = \frac{RT}{P} \, dP \quad (\text{B6})$$

Subtracting equation (B6) from equation (B5) yields

$$RT \, d \ln \left(\frac{f}{P} \right) = \left(V - \frac{RT}{P} \right) dP \quad (\text{B7})$$

Integrating between the pressures zero and P gives

$$RT \left[\ln \frac{f}{P} \right]_{P=0}^{P=P} = \int_0^P \frac{PV - RT}{P} \, dP$$

Because f/P approaches 1 at low pressures

$$RT \ln f = RT \ln P + \int_0^P \frac{PV - RT}{P} \, dP \quad (\text{B8})$$

The integral must be evaluated either graphically or analytically to evaluate the fugacity. Solving the equation of state for $(PV - RT)/P$ and substituting this expression into equation (B8) give

$$RT \ln f = RT \ln P + \int_0^P (B + CP + DP^2) dP$$

or

$$RT \ln f = RT \ln P + BP + \frac{CP^2}{2} + \frac{DP^3}{3} \quad (\text{B9})$$

From equation (B3)

$$RT \ln f = F - F^0 \quad (\text{B10})$$

Substituting equation (B10) into equation (B9) yields

$$(F - F^0)_T = RT \ln P + BP + \frac{CP^2}{2} + \frac{DP^3}{3} \quad (16)$$

which is equation (16) of the main text.

Relative Entropy ($S - S^0$)_T

For a system of constant composition,

$$\left(\frac{\partial F}{\partial T}\right)_P = -S$$

Differentiating equation (16) yields

$$S - S^0 = -\left[\frac{\partial(F - F^0)}{\partial T}\right]_P = -R \ln P - \frac{dB}{dT} P - \frac{dC}{dT} \frac{P^2}{2} - \frac{dD}{dT} \frac{P^3}{3} \quad (B11)$$

Relative Enthalpy ($H - H^0$)_T

Since $F = H - TS$,

$$\begin{aligned} H - H^0 &= (F - F^0) + T(S - S^0) \\ &= RT \ln P + BP + \frac{CP^2}{2} + \frac{DP^3}{3} - T\left(R \ln P + \frac{dB}{dT} P + \frac{dC}{dT} \frac{P^2}{2} + \frac{dD}{dT} \frac{P^3}{3}\right) \\ &= \left(B - T \frac{dB}{dT}\right)P + \left(C - T \frac{dC}{dT}\right) \frac{P^2}{2} + \left(D - T \frac{dD}{dT}\right) \frac{P^3}{3} \end{aligned} \quad (B12)$$

Relative Heat Capacity $(C_p - C_p^0)_T$

The relative heat capacity is simply obtained by differentiation of equation (B12)

$$C_p - C_p^0 = \left[\frac{\partial(H - H^0)}{\partial T} \right]_P = -T \left[\left(\frac{d^2 B}{dT^2} \right) P + \left(\frac{d^2 C}{dT^2} \right) \frac{P^2}{2} + \left(\frac{d^2 D}{dT^2} \right) \frac{P^3}{3} \right] \quad (\text{B13})$$

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